IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Sehyun Kim

Serial No.: 10/786,189

Filed: February 25, 2004

Group No. : 1711

Examiner: Nathan M Nutter

For: Resin Compositions for Producing Biaxially Oriented Polypropylene Films

DECLARATION OF DR. SEHYUN KIM
UNDER 37 C.F.R. § 1.131

I, Sehyun Kim, do declare that I am an inventor of the invention claimed in the patent application titled Resin Compositions for Producing Biaxially Oriented Polypropylene Films that is disclosed and claimed in the above titled application. I am a citizen of the Republic of Korea, and that I reside at Palatine, Illinois 60074. I received a Bachelor's of Engineering in Materials Science and Engineering from Korea University, Seoul, Korea in 1982. I attended the Master's program in Macromolecular Engineering at Case Western Reserve University in Cleveland, Ohio, and received a Master of Science Degree in Polymer Science from the University of Akron, Akron, Ohio in 1985. I received my Ph.D. in Polymer Science from the University of Akron, Akron, Ohio in 1990.

From 1989 to 1990 I was a Postdoctoral Research Associate at the A. E. Staley Manufacturing Company, Decatur, Illinois and the USDA, ARS-National Center for Agricultural Utilization Research, Peoria, Illinois. From 1990 to 1996 I was a Senior Staff Research Chemist for Fina Oil and Chemical Company, Deer Park, Texas. From 1996 to 1997 I was a Product Designer and Technologist for GE Plastics, Washington, West Virginia. From 1998 to 2006 I was employed by Sunoco Chemicals (formerly Aristech Chemicals), Pittsburgh, Pennsylvania, as a Polypropylene Materials Scientist and Intellectual Property

Coordinator. I am currently employed by GLS Corporation, McHenry, Illinois as a Principal Scientist.

I accomplished actual reduction to practice of the claimed compositions of the present invention by July 2001, as shown by this Declaration and the attached Exhibits. Several of the attached Exhibits have been sanitized to remove references to proprietary information.

I conceived this invention in October 1999 as evidenced by the attached e-mail from Dr. Masaki Fujii, dated July 18, 2001, Exhibit A. Attached as Exhibit B is a report from July 16, 2001 outlining the project involving the use of blends of polypropylene homopolymer having a solubles content of less than 3 percent and ethylene propylene random copolymer in biaxially oriented polypropylene films. The data disclosed in Exhibit B corresponds to the compositions and films contained in Example 1 disclosed in my patent application.

I continued work related to my claimed invention throughout 2001 and early 2002. Attached as Exhibit C is a further report from June 6, 2002 documenting this further work related to my invention. Also, in the Abstract of Exhibit C, the previous discovery of the claimed invention is noted. The data disclosed in Exhibit C corresponds to the compositions and films contained in Example 2 disclosed in my patent application.

Based on the work contained in the above documents, we proceeded to prepare a patent application with the help of patent counsel in June of 2002. Work on various drafts of this application proceeded through the summer of 2002. A final draft was approved and filed by counsel on August 27, 2002.

I declare that the foregoing is true and correct, that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that

such willful false statements may jeopardize the validity of the application or any patent

issuing thereon.

Date: October _10_ , 2006

Dr. Sehyun Kim

John Abokhair

From:	Fujii, Masaki [FujiiM@AristechChem.com]
Sent:	Wednesday, July 18, 2001 11:30 AM
To:	Abokhair, John (E-mail)
Cc:	Shamshoum, Edwar S.
Subject:	FW: Invention disclosure and supporting data; BOPP Film Grade PP

disclosure-film.doc PPPD0107006study
IIeffectof RCP...

Dear Mr. Abokhair,

I am sending to you two WORD files attached below; an invention disclosure document "BOPP Film Grade PP" and a research memorandum to support the disclosure. This invention was made by, and the documents were prepared by our Dr. Sehyun Kim. Please record today's date as the date of your receipt of this disclosure.

Actually, Dr. Kim had completed the disclosure document much earlier and put the date and signature on October 20, 1999. If this original hard copy helps to establish earlier date for the invention, I will send it to you by US mail. Please advise.

This invention will be one of those to be discussed at next Sunoco Chemicals IP meeting on 8/20.

Best regards,
Masaki Fujii
Sunoco

> <<disclosure-film.doc>> <<PPPD0107006studyIIeffectof RCP.doc>>

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[EXHIBIT B]
Research Memorandum

Date: July 16, 2001
Project: 3013.02
PPPD # 0107006

BY: Sehyun Kim
Mike Stephans
Nick Karnavas

Subject: STRUCTURE-PROPERTY RELATIONSHIPS IN BOPP (biaxially oriented PP) FILM: STUDY II – Development of an alternative BOPP material to high soluble FF020D

ABSTRACT

In BOPP materials, it had been pointed out that the viscosity of "pseudo-melt" state of the cast sheet at a stretching temperature is important for processability. In an effort to modify the viscosity of such a "pseudo-melt" state of the cast sheet, various polymer blends containing random copolymer were prepared and evaluated with TM Long film stretcher in this study. It was found that the TM Long yield stress decreases with increasing amounts of TR3020 (2.5 % C_2) in D022D having 2.9 % xylene solubles. The addition of TR3020 to D022D up to 20 % did not affect the clarity and mechanical properties of film produced by TM Long film stretcher. Although further investigation is in process, these results to date suggest potential use of homopolymer containing some amounts of random copolymer as an alternative to high soluble film grade material. Realizing Sunoco's multi-reactor lines, i.e., B- and/or C-line, a homo-random polypropylene in situ reactor blend can be produced without sacrificing production rate. It is recommended that a production of FF020D with 4-5 % xylene soluble and 10 –20 % random copolymer having 2.5 % ethylene be seriously considered as an alternative to high soluble (>6 %) FF020D.

KEYWORDS: BOPP (Biaxialy Oriented Polypropylene), random copolymer, TM Long, Xylene Soluble

For a copy of this document, please contact Mary Ellen Shearer at 412-208-8162.

cc: R&T – Pittsburgh (abstract only)

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INTRODUCTION

The BOPP (biaxially oriented polypropylene) film is produced by drawing a cast sheet of isotactic polypropylene below the melting temperature in two directions. A general description of BOPP film production was reported in the previous memo.[1] The BOPP material requires specific characteristics such as relatively larger amounts of xylene solubles, and lower isotacticity, etc.

The BOPP material is often evaluated via the TM Long that is a laboratory film-stretching machine that can generate the elevated temperature stress-strain curve during tensile extension. Such a curve provides useful information about morphological transformations of isotactic polypropylene that occur during drawing. Morphological transformations during drawing are reviewed by Phillips et al.[2]. To screen suitable BOPP materials,

It is well known that isotactic PP (iPP) produced by a Ziegler-Natta (ZN) catalyst has a broad isotacticity and molecular weight distribution, thus exhibiting a broad melting temperature range. The lower the isotacticity of PP, the lower the melting temperature of PP and the better the processability to BOPP film but the poorer the properties of the resulting film. Therefore, there exist a processability-property trade-off in BOPP materials. PP produced by a metallocene catalyst,[3] however, exhibits narrow isotacticity and molecular weight distribution and thus, the melting temperature range is relatively narrow. Unlike PP produced by ZN catalyst, some degree of regio-misinsertion, i.e., "head- to-head" or "tail-to-tail" insertions, of monomer exists in the metallocene isotactic PP (m-iPP). The melting temperature of m-iPP is also affected by the degree of regio-misinsertion in addition to isotacticity. Thus, an iPP of much lower melting temperature than conventional ZN-iPP can be produced with a metallocene catalyst. When employed in BOPP film, much narrower temperature window for drawing was experienced due to the narrow tacticity and molecular weight distribution.[4]

The effect of the addition of m-iPP to ZN-iPP on BOPP film was explored by Phillips et al.[5,6] It was found that the addition of m-iPP to ZN-iPP provides a balance of elevated temperature draw performance and room temperature film properties relative to the ZN-iPP materials. Improved processability of the BOPP film including fewer webs breaks

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[1] S. Kim et al., "STRUCTURE-PROPERTY RELATIONSHIPS IN BOPP FILM: STUDY I," Research Memo, September 30, 1999

[2] R. A. Phillips and T. Nguyen, J. of Applied Polymer Science, 80, 2400 (2001)

[3] E. S. Shamshoum, S. Kim, A. Hanyu and B. R. Reddy, "Properties and Potential Applications of Commercially Produced Metallocene based Syndio- and Iso-tactic Polypropylene," presented at Metallocene '96, Proc. Int. Congr. Metallocene Polym., 2nd (1996), Dusseldorf, Germany

[4] A. K. Mehta et al., SPE RETEC 97 conference, Houston, TX, 1997

[5] see reference #2

[6] T. N. Nguyen et al., WO0011077, Montell Technology Company, July 29, 1999

and drawability at higher line speeds have been claimed by the addition of some amounts of metallocene syndiotactic PP to ZN-iPP.[7] The addition of some amounts of modifier tends to improve processability of iPP and/or properties of the resulting film. The selection of the modifier depends on the desired film properties and availability of modifier.

██. Realizing that the production of high soluble material is not easy because it requires a specific catalyst system and careful handling of powder, an alternative material to high soluble material is sought in this study. The objective of this study is to evaluate the effect of the addition of random copolymer to iPP on processability via TM Long and on film properties. It was hoped that such a homo-random type polypropylene material could be used as an alternative to high soluble FF020D.

EXPERIMENTAL

Some amounts of random copolymer having 2.5 % ethylene (TR3020F) were employed via compounding as given in Table I. D022D powder was used as a base material and a commercial BOPP grade, FF020D, containing relatively large amounts of xylene solubles, e.g., > 4.5 %, has been included for comparison.

Table I
Compounds prepared in this study

2000667	A	B	C	D	E	F
D022	100	95	90	80		
TR3020		5	10	20	100	
FF020D						100

Sheet: 22-23 mil thick sheet was produced using HPM sheet line (L/D = 30) under the following conditions:

Zone	1	2	3	4	Die 1	Die 2	Melt Temp.
Temp. (°F)	400	475	500	500	500	500	505

where the temperature of the chill roll was kept at 110°F (43.3°C).

Density: The density of the extruded sheet was measured in a Techne Density column containing 558 ml H_2O and 322 ml isopropanol mixture in the heavy flask and 327 ml H_2O an 553 ml isopropanol in the light flask.

Stretching: 22-23 mil sheet was stretched to 0.6-0.7 mil film by simultaneous stretching at 6.2 x 6.2 draw ratio with TM Long after 25 sec. pre-heating at a given stretching temperature.

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[7] A. Hanyu et al., US Patent 6207093B1, Mar. 27, 2001, Fina Technology, Inc.

Film properties: The film properties were determined by the method prescribed in ASTM 882.

RESULTS AND DISCUSSION

Characteristics of compounds

The characteristics of compounds containing random copolymer along with homopolymers and random copolymer are given in Table I. A commercial BOPP grade, FF020D, containing relatively large amounts of xylene solubles, e.g., 4.9 %, has been included for comparison.

Table I
Characteristics of compounds containing RCP in comparison to FF020D

2000667[a]	A	B	C	D	E	F
D022	100	95	90	80		
TR3020		5	10	20	100	
FF020D (30H036)						100
MFR	2.0	1.8	1.8	1.8	2.4	2.0
% XS	2.9	2.9	3.1	3.3	5.2	4.9[b]
Mn/1000	64	64.9	65.0	65.7	65.9	66.0
Mw/1000	333	330	328	322	296	349
Mz/1000	930	912	917	874	751	1045
D	5.22	5.08	5.05	4.91	4.49	5.29
D'	2.79	2.76	2.80	2.71	2.54	-
T_m	164.8	164.8	163.1	162.9	149.2	-
T_c	115.0	112.5	112.1	112.0	103.4	-
% X_c	58.7	57.3	57.5	56.3	45.6	53.9[c]

[a] 0.15 Irgafos 168, 0.1 % Irganox 1076, 0.1 % Irganox 1010 and 0.025 % DHOT
[b] Lims #2000884
[c] FF020D (lot 29E081)

It is known that the isotacticity of the insoluble fraction of polypropylene and the amounts of solubles are inversely related and determine the crystallinity of the polymer. Thus, a random copolymer (RCP) that has relatively lower crystallinity with larger amounts of xylene solubles than a homopolymer could modify (or decrease) the overall crystallinity when added to homopolymer. Table I indicates that the addition of RCP slightly increases the amounts of xylene solubles, decreases the overall crystallinity and the recrystallization temperature. Addition of 20 % RCP was not, however, enough to decrease the overall crystallinity of the compound to the same level as that of FF020D. Based on the additive rule, it appears that about 40 % RCP is required to have a comparable overall crystallinity to FF020D.

It is noted that the molecular weight distributions of all the polymers are comparable within the limit of experimental error. Therefore, the effect of MW and/or MWD on the stretchability and film properties has been ignored in this study.

Cast sheet and TM Long films

Table II gives the density of the cast sheet, TM Long yield stress and film properties while Figures 1 and 2 show the dependence of TM Long yield stress on the stretching temperature and the cast sheet density, respectively. In accordance with the overall crystallinity of the compound, the density of the cast sheet also decreases with increasing amounts of RCP. The TM Long yield stress decreases with increasing stretching temperature and/or with decreasing the density of the cast sheet as shown in Figures 1 and 2.

Table II
Density of sheet stock and TM Long yield stress

LIMS #2000-	667A	667B	667C	667D	667E	884A
	D022	5% RCP	10 % RCP	20 % RCP	TR3020	FF020D (30H036)
Density[a]	0.9028	0.9025	0.9017	0.9017	0.8957	0.8988
TML[b] yield stress (psi)						
@ 280°C	505	494	486	458	125	404
@ 290°C	377	390	378	319	38	294
@ 300°C	258	251	234	199	-	174

[a] cast sheet; [b] TM Long

Figure 1
TM Long Yield Stress of various compounds in comparison to FF020D
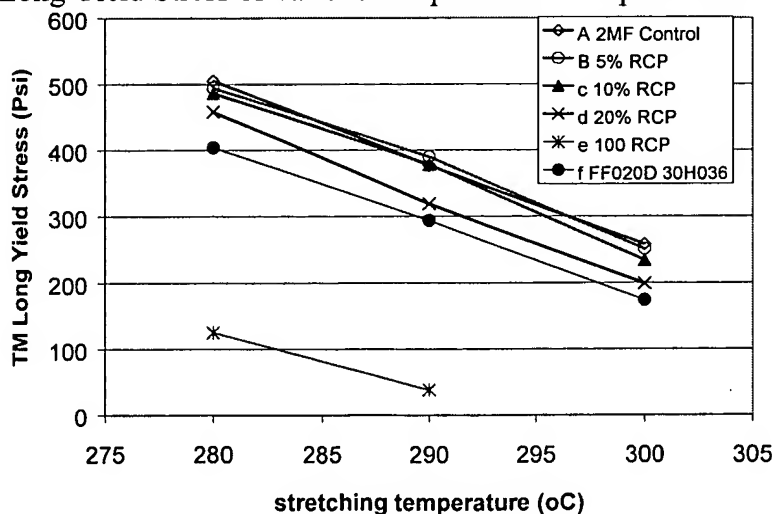
It is noted that FF020D that has 4.9 % xylene solubles exhibits about 100 psi lower TM Long yield stress than D022 that has 2.9 % xylene solubles irrespective of the stretching temperature. TR3020 that has 2.5 % ethylene and 5.5 % xylene solubles has significantly lower TM Long yield stress than FF020D. It can be attributed to the lower melting temperature and overall crystallinity of random copolymer along with larger amounts of xylene solubles than homopolymer. As was stressed in the previous memo,[8] these results imply that the crystalline state at the stretching temperature dictates the TM Long yield

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[8] see reference #1.

stress. It is noted that the crystalline state of a polypropylene at a stretching temperature predominantly affects the viscosity of the "pseudo-melt" (because the polymer is partially melted) along with molecular weight.

Figure 2
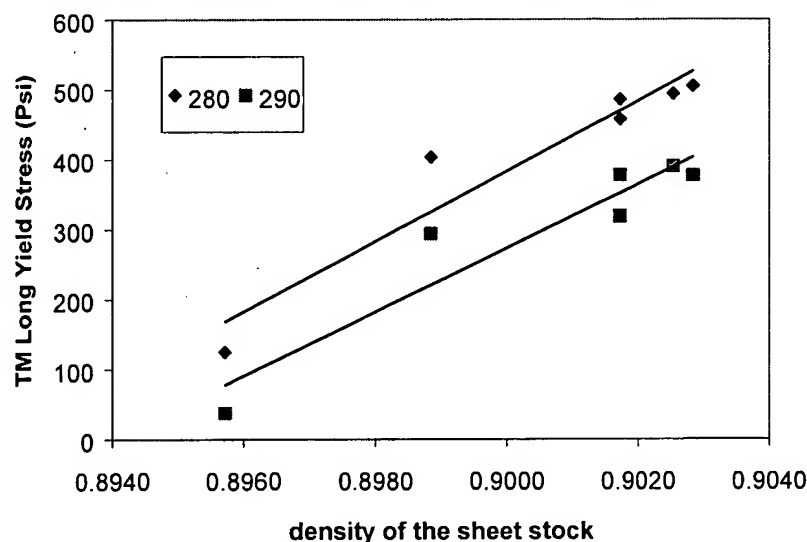TM Long yield stress stretched at 280 and 290°F as a function of cast sheet density

Table III gives the properties of film produced with TM Long stretcher. Although some error exist in these results, the tensile properties and haze of the compounds appear to be comparable to those of homopolymer, i.e., FF020D, up to 20 % addition of random copolymer. These results to date suggest that the homo-random polypropylene can be employed as an alternative BOPP material replacing high soluble homopolymer.

Table III
Properties of film produced at 280°F by stretching at 6x6 ratio

LIMS #2000-	667A	667B	667C	667D	667E	884A
	D022	5% RCP	10 % RCP	20 % RCP	TR3020	FF020D (30H036)
Tensile stress (kspi)	27.1	31.4	31.1	30.3	21.9	27.1
Tensile strain (%)	63.2	70.2	72.4	74	59.9	69
Modulus (kpsi)	367	370	370	254?	363	332
Haze	0.63	0.63	0.68	0.63	0.67	0.65

It is known that it is difficult to produce a homopolymer containing xylene solubles fractions higher than 6 % because a specific catalyst system as well as careful handling of polymer powder in the reactor are required. In general, the large amounts of xylene soluble in the polypropylene become sticky and often cause agglomeration of polymer powder in the reactor, disrupting continuous production at the plant. These results obtained in this study, however, provide some insight to take advantage of multiple reactors in series, i.e., B- or C-line. The fact that the addition some amounts of random copolymer to a conventional homopolymer decreases overall crystallinity and melting

temperature suggest a potential use of homopolymer-random copolymer at a desired ratio as an alternative to high soluble FF020D. It is expected that such a homo-random polypropylene in situ blend can be produced on B- or C-line without sacrificing production rate.

CONCLUSION AND RECOMMENDATIONS

Various polymer blends containing random copolymer were prepared and evaluated with TM Long film stretcher in this study. The results were compared to a conventional BOPP film grade material, FF020D. Although further investigation is in process, it may be concluded from this study that the overall crystallinity, and thus the density of the cast sheet, that is critical in BOPP material can be modified by adding random copolymer instead of producing larger amounts of xylene solubles.

It is recommended that a production of FF020D with 4-5 % xylene soluble and 10 –20 % random copolymer having 2.5 % ethylene be seriously considered as an alternative to high soluble (>6 %) FF020D.

ACKNOWLEDGEMENTS

Many thanks to M. Stephans of Application Laboratory for compounding, TM Long and film mechanical Test, and to R. Peratt and J Wall of Analytical Laboratory for xylene solubles, HSEC and for ADSC, respectively.

[EXHIBIT C]

R&T PROJECT REPORT

NOVEL BOPP FILM GRADE MATERIAL

Sehyun Kim
Mike Stephans

June 6, 2002

ABSTRACT

BOPP film manufacturers have long sought a material that provides a stiffer oriented film while maintaining acceptable stretchability. This study is an effort to develop such a material by using melt blends of a high crystalline PP (HCPP), F050HC, and a random copolymer (RCP), TR3005. Through this study, the previous discovery that the addition of RCP to a homopolymer, which has relatively small amounts of xylene solubles and is not easily stretchable, facilitates the stretchability of homopolymer was confirmed. The TM Long yield stress indicates that a HCPP can be modified to be stretchable under the conventional processing conditions. Furthermore, the films made from the blend containing HCPP and RCP exhibit improved properties over FF029A in addition to acceptable stretchability. Since a homopolymer that contains 15-30% RCP can be produced "in-situ" in the plant without sacrificing production rate, which is potentially increasing, it is recommended that a HCPP material containing random copolymer having 2.5% ethylene be produced in the plant and be evaluated at the customer sites. Unfortunately, BOPP film manufacturers are not willing to evaluate a conventional BOPP material such as FF029A without significant incentives. However, the material developed in this study, which maintains improved properties over a conventional BOPP grade material, could open doors to Sunoco.

KEYWORDS: BOPP (Biaxially Oriented Polypropylene), random copolymer, FF050HC, blend, FF029A

For a copy of this document, please contact Darlane Abel at 412-208-8138.

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BACKGROUND, PURPOSE, & COMMERCIAL INCENTIVE

The previous study (1) suggested an alternative material to high soluble homopolymer for BOPP film application. This alternative material is composed of a low soluble homopolymer and a random copolymer (RCP) of 2.5% ethylene content. However, the stretchability of such a material and the properties of its TM Long film proved to be comparable to a high soluble homopolymer (FF020D). It was proposed that such a polymer could be produced in situ in a series of reactors such as B- or C-line without difficulty, with a potentially higher production rate.

BOPP film manufacturers have long sought a material that can produce a stiffer film, which has acceptable stretchability and thus, allows the film manufacturers to produce thinner gauge films, thereby decreasing their material cost. Although a high crystalline PP (HCPP) provides high stiffness, it has not been employed in oriented film application because of its limited stretchability on a tenter frame. However, the concept employed in the previous study suggests a potential use of a HCPP in the oriented film. In this study, a HCPP, F050HC, has been employed as a base homopolymer and TR3005 having 2.5% ethylene a RCP. The objectives of this study were to confirm the concept explored in the previous study and to develop a novel BOPP material in hopes that such a homo-random type polypropylene material with improved film properties, such as acceptable stretchability despite stiffness, could be possible.

In pursuing the concept employed in this study and previous one, there are at least two commercial incentives. Since the material developed in this study does not require the large amounts of soluble (5-6%) necessary for a conventional BOPP film grade material, the material would be plant friendly. For example, the material yields no powder agglomeration, no donor level change while at a potentially improved production rate. Also, the stiffer film grade material that has suitable stretchability on a tenter frame would allow more business opportunities for Sunoco at larger BOPP film manufacturers such as ██ and ████████.

EXPERIMENTAL MATERIALS & METHODS

Materials

A random copolymer having 2.5% ethylene (TR3005) was melt blended with F050HC via compounding as given in Table I. A conventional BOPP material, FF029A, designed for the core material of clear film, was used as a control.

Table I
Compounds prepared in this study

2100944	A	B	C	D
F050HC	100	85	70	
TR3005		15	30	
FF029A (31J026)				100

Characterization

ADSC (Annealed Differential Scanning Calorimetry)

Polymer was melted at 230°C for 5 minutes and cooled to 0°C at a rate of 10°C/min while recording recrystallization exotherm. Then, the sample was heated to 190°C at a rate of 10°C/min to record the melting endotherms.

Thermal Fractionation

The polymer melt was cooled to 170°C at a rate of 20°C/min, followed by isothermal crystallization process during which the sample was held for 4 hrs. The isothermal crystallization process continued to decrease to 130°C at 10°C decrement. The temperature of the sample was then decreased to 0°C, and the sample was analyzed as it was heated to 200°C at a rate of 10°C/min. to record the melting endotherm.

NMR (Nuclear Magnetic Resonance) Spectroscopy

The 75 MHz ^{13}C-NMR spectra were recorded on the xylene insoluble fractions.

Preparation of Sheet

22-23 mil thick sheet was produced using HPM sheet line (L/D = 30) under the following conditions:

Zone	1	2	3	4	Die 1	Die 2	Melt Temp.
Temp. (°F)	400	475	500	500	500	500	505

where the temperature of the chill roll was kept at 110°F (43.3°C).

Density (ASTM 1505)

The density of the extruded sheet was measured in a Techne Density column containing 558 ml H_2O and 322 ml isopropanol mixture in a heavy flask and 327 ml H_2O an 553 ml isopropanol in a light flask.

TM Long Film

22-23 mil sheet was stretched to 0.6-0.7 mil film by simultaneous stretching at 6.2 x 6.2 draw ratio with TM Long after 25 sec. pre-heating at a given stretching temperature. The yield stress was measured while stretching the cast sheet.

Film Tensile properties

The film tensile properties were determined by the method prescribed in **ASTM 882**. The strips (1" x 8") from TM Long film were used to determine the tensile properties. Although ASTM recommends 10" grip separation and 1 in/min crosshead speed for the measurement of tensile modulus, 4" grip separation was employed due to the size of the TM Long film. Accordingly, the crosshead speed was adjusted to 0.4 in/min. For all other tensile properties, the crosshead speed was 2 in/min. At least 5 specimens were tested.

Optical properties

Optical properties such as transparency, haze and clarity of the film were evaluated by the method prescribed in **ASTM 1003** (Haze and % transmittance) and **ASTM 1746** (clarity).

Gloss

Gloss was measured at the 3 different angles, 20, 45 and 60 degree by using the method described in **ASTM 2457**, where 60 deg. is recommended for intermediate gloss films, 20-deg. for high gloss films and 45-deg. for intermediate and low gloss films.

Shrinkage measurement (ASTM D2732)

A rectangular cutout (3.9"x 3.9") from TM Long film was placed in a "Free Shrink" holder such that the cutout is free from contact with the edge of the holder. Then, the holder was immersed in an oil bath for at least 10 seconds at a given temperature in order for the material to come to thermal equilibrium and undergo maximum shrinkage. The holder was removed from the oil bath and quickly immersed in oil at room temperature. After at least 5 seconds, the sample was removed from the oil. After removing the remaining oil from the specimen, the dimension of the specimen was measured and the shrinkage was calculated using the equation below.

$$\% \text{ shrinkage} = (L_o - L_f)/L_o \times 100$$

where L_o is the initial length and L_f length after shrinking.

RESULTS AND DISCUSSION

Characteristics of compounds

The characteristics of materials employed in the study are given in Table II. A commercial BOPP grade, FF029A that contains relatively large amounts of xylene solubles, e.g., 5.8%, has been included for comparison. As reported in the previous report (1), a RCP that has 2.5% ethylene has relatively lower crystallinity and larger amounts of xylene solubles than a homopolymer. Therefore, when added to homopolymer, a RCP could modify, i.e., decrease, the overall crystallinity. Table II confirms that the addition of RCP to a homopolymer slightly increases the amounts of xylene solubles, decreases the overall crystallinity and the recrystallization temperature. It is noted that the blend of F050HC with 30% TR3005 has a slightly higher crystallinity than FF029A. Although FF050HC employed in this study does not have the isotacticity (% mmmm) high enough as a HCPP (2,3), it has a higher crystallinity than FF029A, mainly due to much smaller amounts of xylene solubles. Furthermore, the average meso run length, Nm, of HCPP and its blend with a RCP is much higher than that of FF029A.

The molecular weight and distributions of all the polymers are comparable within the limit of experimental error, although the fractional MFR TR3005 was added to 5 MFR

F050HC. Therefore, the effect of MW and/or MWD on the stretchability and on the film properties has been considered insignificant in this study.

Table II
Characteristics of compounds containing RCP in comparison to FF029A

2100944	A	B	C	D
	F050HC	15 % TR3005	30% TR3005	FF029A (31J026)
MFR	6.2	4.6	3.7	3.0
% XS	**1.73**	**2.28**	**3.12**	5.82[a]
T_m	163.7	162.2	159.3	159.1
T_c	118.1	115.1	112.9	112.6
% X_c	61.9	58.6	55.2	53.3
mmmm	96.86	96.53	-	95.23
mr + rm	0.89	0.99	-	1.55
Nm[b]	223	200	-	126.9
Mn/1000	53.5	63.2	65.8	50.4
Mw/1000	252	278	283	257
Mz/1000	779	819	838	988
D	4.7	4.4	4.3	5.1
D'	3.1	2.9	3.0	3.8

[a] LIMS 2100735; [b] average meso run length

Cast sheet and TM Long films

Table III gives the density of the cast sheet, TM Long yield stress and film properties while Figures 1 and 2 show the dependence of TM Long yield stress on the stretching temperature and the cast sheet density, respectively.

Table III
**Density of sheet stock and TM Long yield stress**

2100944	A	B	C	D
	F050HC	15% TR3005	30% TR3005	FF029A
Density[a]	0.9043	0.9034	0.9026	0.9029
TM Long yield stress (psi)				
@ 280°C	779[b]	644	549	519
@ 290°C	594	496	418	390
@ 300°C	445	365	281	253

[a] cast sheet; [b] the film tore during stretching after yield.

In accordance with the overall crystallinity of the materials, the density of the cast sheet decreases with increasing amounts of RCP as does the TM Long yield stress as shown in Figures 1 and 2. While the TM Long film of FF050HC tore after yielding when stretched at 280°F, the blend containing 15% random copolymer did not tear when stretched. It is noted that although the blend that conains 30% random copolymer has a slightly lower density than FF029A, its TM Long yield stress is higher as shown in Figure 2. Since the TM Long yield stress depends on the density, i.e., crystallinity, of the cast sheet at the stretching temperature, it appears that the blend containing 30% random copolymer should have a higher density at the stretching temperature than FF029A does.

Figure 1
TM Long Yield Stress of various compounds in comparison to FF029A
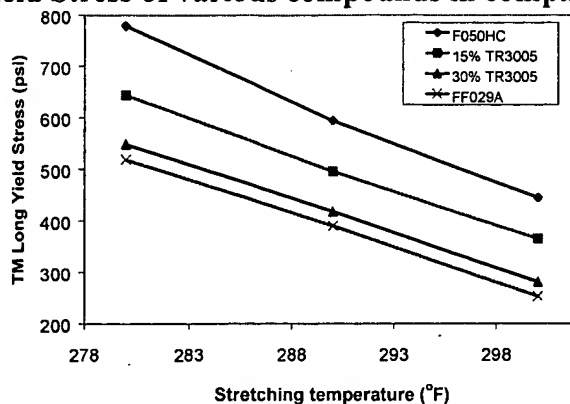
Figure 2
TM Long yield stress stretched at 280 and 290°F
as a function of cast sheet density
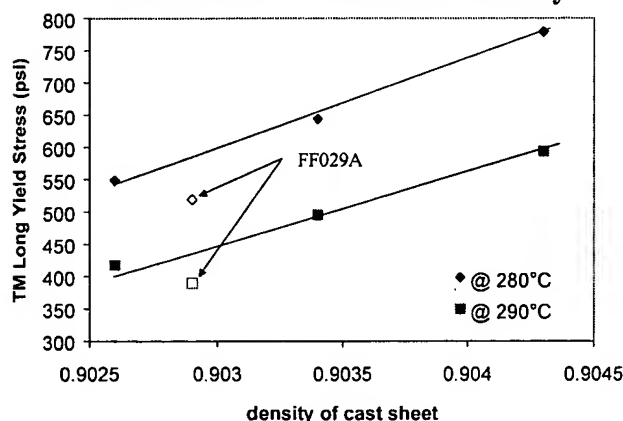
The properties of film produced at 3 different temperatures with TM Long stretcher are given in Table III and depicted in Figures 3-8. Although some errors exist in these results, Table III may be summarized as follows:

• The TM Long films produced from the blends exhibit higher tensile properties than those produced from FF029A.

• Haze and % transmittance of the film produced from the blends at 280 and/or 290°F are comparable to those produced from FF029A. However, when stretched at 300°F, the film produced from FF029A is much hazier than those from the blends.

• The 45-degree gloss varies depending upon the stretching temperature.

• The shrinkage of the film from the blends is slightly lesser than that from FF029A.

Table III
### Properties of TM Long film produced at various temperatures

2100944	280°F A	B	C	D
	F050HC[a]	15% TR3005	30% TR3005	FF029A
Haze	-	0.90	0.58	0.63
Transmittance (%)		94.5	94.4	94.5
Clarity	-	97.4	98.1	98.0
Gloss 20	-	36.1	27.2	41.0
45	-	93.1	90.3	93.7
60	-	129.7	114.2	114.2
Tensile stress (kspi)	-	31.6	32.4	33.4
Tensile strain (%)	-	68.6	70.0	72.0
Modulus (kpsi)	-	524	471	448
Shrinkage (%)	-	17.5	19.9	19.5
	290°F			
Haze	-	0.72	0.77	0.61
Transmittance (%)		91.9	92.6	92.2
Clarity	-	97.8	97.4	98.9
Gloss 20	-	47.1	89.4	84.3
45	-	86.2	86.2	91.7
60	-	127.2	126.3	126.4
Tensile stress (kspi)	33.4	35.6	33.4	32.3
Tensile strain (%)	75.0	77.3	80.0	72.1
Modulus (kpsi)	601	579	561	496
Shrinkage (%)	-	16.16	19.65	18.17
	300°F			
Haze	1.58	2.63	2.5	6.08
Transmittance (%)	91.2	90.9	91.1	87.2
Clarity	95.3	90.5	91.3	87.1
Gloss 20	44.5	67.1	47.3	46.7
45	88.9	85.8	86.3	79.3
60	113.9	114.4	109.1	103.8
Tensile stress (kspi)	29.5	27.2	29	24.7
Tensile strain (%)	83.6	65	81.5	66
Modulus (kpsi)	536	470	521	356
Shrinkage (%)	8.3	10.1	9.1	10.1

[a] film broke after yield.

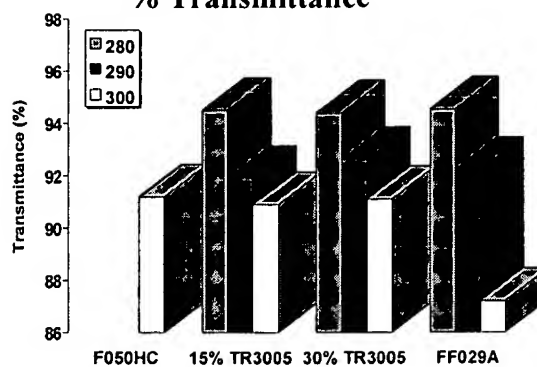### Figure 3
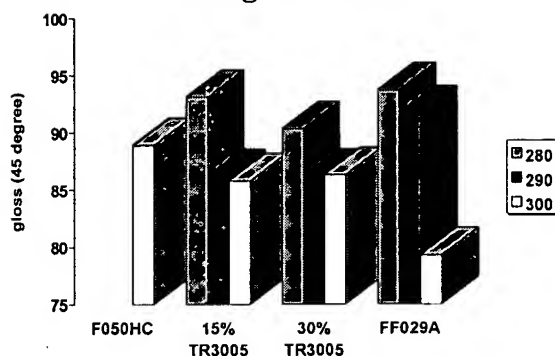### Tensile Stress
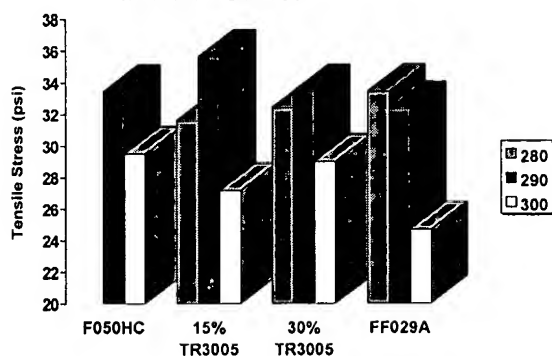
Figure 4
Tensile Modulus
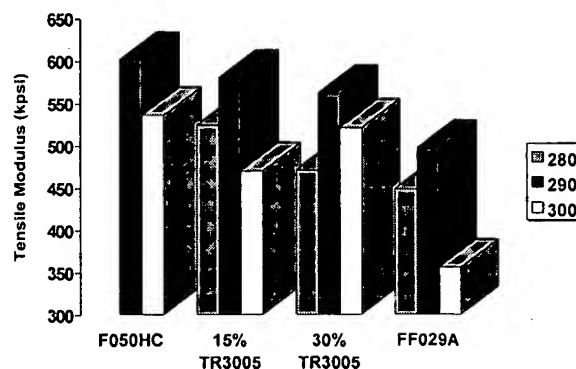
Figure 5
Haze
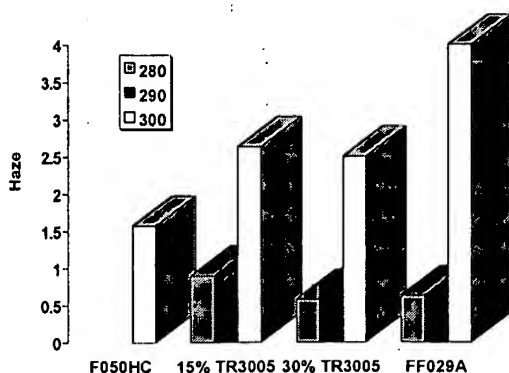
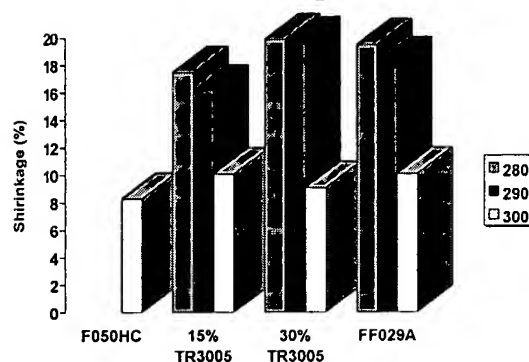**Figure 6**
**% Transmittance**

Figure 7
45 degree Gloss

Figure 8
Shrinkage

Thermal Fractionation

As discovered in the previous reports (4-6), how well a material stretches on a tenter frame depends on the shape of endotherm recorded from the thermal fractionation. Thus, the thermal behavior of the materials employed in this study has been evaluated via the thermal fractionation method as shown in Figure 9. Interestingly, the melt blend of FF050HC with 30% RCP exhibited a similar endotherm to FF029A that ran very well both on a pilot tenter line at ████ and on a commercial tenter line in ████ .

Figure 9
Thermal fractionation endotherms of HCPP (FF050HC) and its blend with 30% RCP in comparison to FF029A (31J026)
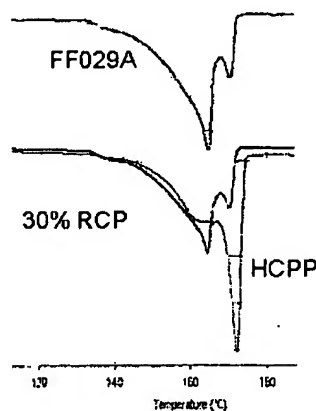
CONCLUSIONS, RECOMMENDATIONS, & COMMERCIAL IMPLICATIONS

In this study, various polymer blends and their TM Long films of a HCPP, FF050HC, and a RCP, TR3005, were prepared and evaluated in comparison with a commercial BOPP grade material, FF029A. The following conclusions may be drawn from this study:

- This study confirms the previous discovery that the addition of RCP to a homopolymer, which has relatively small amounts of xylene solubles and is not easily stretchable, facilitates the stretchability of homopolymer.

- The concept introduced in this study is especially advantageous to a stiffer film since a high crystalline PP can be modified to be stretchable under the conventional processing conditions.

- The films produced from the blend containing HCPP and RCP exhibit improved properties over FF029A.

As proposed in the previous report, a material containing 10-30% RCP can be produced "in-situ" in the plant without sacrificing production rate, which is potentially increasing. It is recommended that a HCPP material containing 15–30% random copolymer having 2.5% ethylene be produced in the plant and be evaluated at the customer sites. Most importantly, BOPP film manufacturers are not willing to evaluate a conventional BOPP material such as FF029A without significant incentives. However, the material developed in this study, which maintains improved properties over a conventional BOPP grade material, could open doors to Sunoco.

ACKNOWLEDGEMENTS

Many thanks to M. Stephans of Application Laboratory for TM Long and film properties and to R. Peratt, J. Wall and M. Brethauer, HSEC, DSC (thermal fractionation) and xylene solubles, extracting components. Also, thanks go to Dr. S. Zhang for NMR.

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Polypropylene Handbook

Polymerization, Characterization, Properties, Processing, Applications

Edited by
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HANSER

Hanser Publishers, Munich Vienna New York

Hanser/Gardner Publications, Inc., Cincinnati

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Figure 1
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* Montell Poly

Figure 1.3 Addition of propylene to the growing PP chain in the same (A) and opposite (B) hand

A. Same hand

B. Opposite hand

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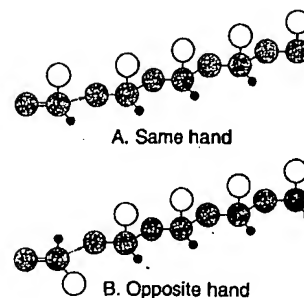iil regarding these
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The degree of stereoregularity (and consequent crystallinity) among conventional PPs varies considerably. Even homopolymers, where the room temperature xylene solubles level approximates the atactic content, are available from as little as 1% xylene solubles to about 20%. These variations are usually due to the effectiveness of the polymerization catalyst, but the production process also can have some effect. One of the major driving forces in the PP industry has been the ability to improve the process as a result of improvements in the catalysts. That is addressed in Chapters 2 and 8.

Beyond homopolymers, there is a wide range of copolymers and terpolymers, usually of ethylene and butene, of two types: random and impact. Random copolymers typically contain up to 6% (by weight) of ethylene or other comonomers inserted at random within the chain, which reduces the crystallinity and the melting point by introducing irregularities into the chain. Random copolymers are used where clarity, lower melting point, or lower modulus is desirable. Impact copolymers, also known as heterophasic copolymers, usually contain up to about 40% ethylene-propylene rubber (EPR), intimately dispersed within the matrix, usually homopolymer. As the EPR is usually about 50% ethylene, this translates into a 20% ethylene level on the total product, a more widely used description. As implied in the name, those copolymers are used where impact strength is important, especially at low temperatures. The compositions, molecular weights, amounts, and morphologies of the dispersed EPR and continuous homopolymer phases are crucial to having an effective impact copolymer. Chapters 3, 5, and 6 provide more details.
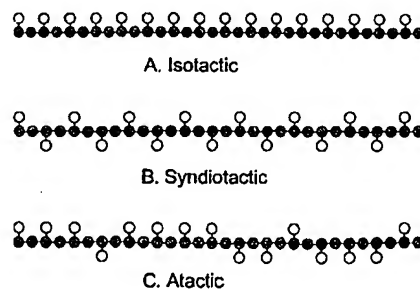

A. Isotactic

B. Syndiotactic

C. Atactic

B) addition of propy-

Figure 1.4 Schematic illustrations of isotactic (A), syndiotactic (B), and atactic (C) PP

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As might be expected, the extent of impact enhancement increases with elastomer content [27, 28, 29]. In commercial products, levels of elastomer do not usually exceed about 20%, since the addition of greater quantities results in an undesirable softening.

The effect of elastomer particle size is important because it determines the number and spacing of particles at a given concentration. Impact characteristics can be influenced by elastomer particle size, principally through the effect on initiation and termination of crazing and shear yielding [30]. It is recognized that, for a particular polymer pair, there exists a critical particle size that yields optimum toughness. That optimum is about 0.4 μm for PP/EPR.

Martuscelli and co-workers reported the influence of EPR copolymer structure and composition on melt rheology, phase morphology, and impact fracture behavior of PP/EPR blends [29, 31 - 33]. It was found that the degree of dispersion of EPR in the PP matrix was a crucial factor for good impact. The degree of dispersion was, in turn, determined mainly by the melt- phase viscosity ratio (viscosity of dispersed phase/viscosity of matrix).

The range of particle sizes effective for PP toughening varies with test temperature. For the test at room temperature, a quite wide range is effective. Below the T_g of PP, a narrower range is needed, and approaching the T_g of the elastomer, the range is narrowest.

The sensitivity of impact enhancement to the T_g of the elastomer can be clearly demonstrated by the dependence on the test temperature [26]. Below the T_g of the elastomer, it is ineffective. Accordingly, for adequate impact at a particular temperature, the T_g of the elastomer must be below that temperature.

Good adhesion between elastomer particle and PP matrix is also believed to be essential for the effectiveness of elastomer toughening. For example, polyisoprene is not a good impact modifier for PP due to the wide difference in solubility parameters, and thus poor adhesion, between it and PP [27]. However, a significant improvement in the impact strength of this polymer system was achieved by the use of a grafting additive to promote interfacial adhesion [34].

The C_2/C_3 content of the EPR affects the blend in different ways. At high C_3 levels, the high T_g would control, and poor impact would result, although miscibility or interfacial adhesion should be adequate, and some PP crystallinity in the EPR would reduce shrinkage stresses in the PP matrix. As C_2 content increases, PP crystallinity disappears and T_g drops, but shrinkage stresses remain (see Sections 5.5.2 and 3.5.5). At still higher C_2 levels, polyethylene (PE) crystallinity develops, and impact resistance reaches a maximum. The highest C_2 levels reduce the interfacial adhesion, and impact level drops again. The optimum concentration, which is quite sharp, is around 50 to 60 mole% C_2 [35]. Thus, the dispersed elastomer phase must be sufficiently immiscible with the matrix to maintain phase separation, yet adequately miscible to provide for strong adhesion between two phases.

5.4   Impact-Modified PP

Polypropylene homopolymer, while having a number of valuable properties and economic benefits, exhibits a poor low-temperature impact resistance. Such a shortcoming is due to its relatively high glass transition temperature (T_g), about $-15\,°C$. Incorporation of a soft,

elastomeric phase as a toughening agent is an effective way to improve the low-temperature impact strength of PP. Various elastomers have been used as impact modifiers, but EPR is the most common. The resulting PP/elastomer polymer systems are normally multiphasic, with the elastomer as the minor, dispersed component. Impact enhancement is usually achieved at the cost of a reduction in modulus and strength. We refer to blends with up to about 20% rubber as impact-modified PP.

5.4.1   Performance

Having about the same rubber content and particle size (in the fabricated part) as a reactor-prepared heterophasic copolymer, the impact-modified PPs display the same ranges of modulus, impact strength, and other basic end-use properties, which are discussed in Chapter 6. However, other additives may be added to the blends with virtually no cost penalty. Thus, pigmented, antistatic, and special stabilization and other additive compositions are readily accommodated in the compounds. In addition, the scale of the reactor operation limits its products to those applications commanding large volumes only, while compounded products may be prepared on a much smaller scale, and in a shorter time frame. In this sense, compounded blends are more specialty products than reactor copolymers.

5.5   Thermoplastic Olefins

Thermoplastic olefin elastomers (TPOs) are basically blends of noncross-linked elastomers with polyolefin polymers such as PP or PE. The distinction between an impact-modified PP and a TPO is somewhat arbitrary; for this discussion, we consider rubber levels over about 20% to be TPOs. We will concentrate on binary blends of PP with EPR or EPDM, and ternary blends of PP, PE, and EPR or EPDM, as they constitute the largest group of TPOs in the market. In addition, the recent advance of in-reactor TPOs will be addressed.

5.5.1   EPR Blends

5.5.1.1   Morphology

In PP/EPR blends, the multiphasic morphology was observed by microscopy and dynamic mechanical tests [36 - 40]. In microscopic studies, three types of dispersed morphology were observed at different compositions. When EPR forms the minor phase, the average size of dispersed EPR particles depended largely on the relative viscosity between PP and EPR; the morphology of a very fine and uniform distribution of the EPR particles could be obtained when the two component polymers had similar melt viscosities. In the intermediate composition range, the blends with a lower viscosity EPR showed cocontinuous morphology in a wider range of concentration than those with higher viscosities. At high elastomer content, as expected, EPR forms the matrix and PP droplets are dispersed in it. Dynamic

mechanical analysis (DMA
identical to the pure compo
spite of the intimate ming
PP/EPR blends are also
morphological descriptions
TPOs appear in Section 3.5

In injection molding c
observed within the cross s
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5.5.1.2   Properties

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mechanical analysis (DMA) showed that the transition temperatures of the blends were identical to the pure components, indicating total incompatibility between PP and EPR, in spite of the intimate mingling of the phases. The rules controlling the morphologies in PP/EPR blends are also applicable to PP/EPDM systems [36, 37, 40, 41]. Detailed morphological descriptions of impact-modified PP, reactor-based impact copolymers, and TPOs appear in Section 3.5.

In injection molding of these blends, two distinct morphological layers are generally observed within the cross section [42, 43]. Near the top surface, there exists a shear zone having an elongated elastomer phase. Elastomer particles in this zone are highly stretched and oriented with the injection direction as a result of high shear rates near the wall during mold filling coupled with a high cooling rate. The shear zone is followed by a core zone of a large number of randomly sized spherical elastomer particles. It is also possible that, during injection molding, some elastomer particles in the core zone are elongated by flow, and spherulites nucleate along rows due to the shear. However, the slower cooling rates of polymer melt in this region allow the elastomeric inclusions time to relax, yielding spherical droplets. The morphology of the shear zone has significant effects on surface character, while the physical properties depend more on the morphology of the core zone. Further description of the effects of molding may be found in Section 3.6.

The crystallization behavior of PP-based blends containing EPR or EPDM has also been reported. A substantial increase in the number of nuclei in the blends with increasing elastomer content in the system has been found [8, 44 - 47]. The change in nucleation density was first attributed to nucleation activity by the elastomer on the PP. More recent work has shown that the increased nucleation is the result of a greater number of heterogeneous nuclei (inorganic residues and contaminants) that migrate from the EPR phase into PP during the mixing process. Using EPR copolymers with a reduced number of heterogeneities, D'Orazio et al. reported that the effects of EPR on nucleation behavior of PP/EPR blends disappeared [9].

Although the rubber is clearly immiscible with PP, the character of the PP spherulites has been shown to be affected by the rubber addition. Melting points and heats of fusion (PP basis) were lower, and the spherulites were more irregular in texture and boundaries. At the same time, the crystallization temperatures are raised, based on the nucleation mentioned above. Unfortunately, nucleation, by raising the crystallization temperature, would work to reduce impact; smaller, but more dense and more brittle spherulites would result. Many investigators confuse this behavior with the results of higher quench rate, which gives the smaller, less well-defined, and therefore tougher spherulites of the mesomorphic (smectic) form of PP. Thus, the observation of less regular, lower melting spherulites in EPR/PP blends is more likely to explain the improved impact than nucleation.

5.5.1.2   Properties

In a tensile test, results obtained from a large number of blends have shown that elastic modulus is not very sensitive to structural differences [48]. In fact, its value depends almost entirely on composition and moduli of constituent components. Young's modulus of PP/elastomer systems, as expected, decreases with increasing the EPR or EPDM content [41, 49 - 51]. Chemical modification of EPR or PP by maleic anhydride grafting did not cause any significant effect on concentration dependence of elastic modulus.

Tensile yield strength of the PP/elastomer systems decreases monotonically with increasing EPR or EPDM content due to the reduction of the effective matrix cross section introduced by the elastomer phase [41, 49]. The engineering yield strength of the PP/elastomer blends is a predictable function of elastomer content using the Nicolais–Narkis equation [52]. Since the elastomer does not exhibit the characteristic yielding behavior of the thermoplastics, above a certain elastomer content, a distinct yield point cannot be defined.

5.5.2   Ternary Blends of PP, PE, and EPR

The PP/EPR binary mixtures often exhibit a behavior known as "blushing," where a whitening occurs when the molded part is deformed. It has long been known that addition of HDPE to the PP/EPR blends can reduce this tendency [53, 54]. Studies of the morphology of these ternary mixtures revealed that the HDPE tended to gather within the EPR particles [55 - 61]. Thus, in PP-rich ternary blends, HDPE and EPR have an affinity for each other. They tend to combine within PP to form a characteristic morphology with HDPE particles surrounded by an elastomer shell. About 20 vol% of EPR could accommodate 20 to 30 vol% of HDPE [40, 62].

As illustrated in more detail in Section 3.5.5, the HDPE addition provides a better match between the matrix and dispersed phase shrinkages. The low shrinkage of the amorphous EPR normally creates tensile stresses in the high-shrinking PP matrix during cooling, allowing cracks and crazes to form later at low levels of strain. The HDPE induces higher shrinkage in the dispersed phase particles, lowers the stresses in the PP matrix, and reduces the tendency to form voids or crazes when the item is deformed. The effectiveness of this solution is not sensitive to the source of HDPE; either reactor or compounding can be satisfactory, provided the usual concerns about dispersion and particle size are observed in the compounding approach.

5.5.3   In-Reactor Thermoplastic Olefins

Thermoplastic olefins are traditionally manufactured by mechanical blending. With the development of new catalyst systems and polymerization technology, it is now possible to produce these kinds of blends directly in the reactor [63 - 65]. In-reactor TPOs have several important advantages over conventional, mechanically blended TPOs, namely:

- Products are polymerized directly from monomers. The decreased variability in raw materials imparts better material consistency.
- Fewer manufacturing steps are required to produce materials directly from the reactor. Therefore, cost savings are possible.
- Elastomers are finely dispersed in the olefin matrix. As a result, the in-reactor TPOs exhibit improved physical properties and melt uniformity.
- A wider range of elastomeric compositions are possible, as the viscosity ratio does not restrict the selection as severely as in blends.

Besides the obvious adv controlling the chemical str reactor. Therefore, composit possible can now be produce

5.5.4   Performance (

TPOs are a class of material of performance characteris properties for commercial T summarized in Table 5.1.

Applications for these r moldings to commercial re performance capability.

1. Mechanical properties:
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   PP copolymers are avai
   automotive body panels
   the entire property rang
2. Thermal properties: De
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   grades can endure long
   properties. The combi
   suitable for wire, cable,
   temperature properties (
   TPOs suitable for man:
3. Environmental: As witl
   and alkalis, especially
   phase. They do not abs
   They can be formulate

Table 5.1 Selected Property I

Property
Melt flow
Hardness
Flexural modulus
Tensile strength
Elongation
Gardner impact at −20 °F

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; matrix cross section
ield strength of the
using the Nicolais–
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the in-reactor TPOs

cosity ratio does not

Besides the obvious advantages mentioned above, the new technology is also capable of controlling the chemical structure and physical properties of the constituent polymers in the reactor. Therefore, composition and formulation not previously economic or even physically possible can now be produced. Details of this technology appear in Sections 3.5.6 and 7.1.8.2.

5.5.4   Performance of TPOs

TPOs are a class of material with a broad range of compositional variety leading to a diversity of performance characteristics, ranging from soft, flexible to rigid and tough. Selected properties for commercial TPOs including both mechanical blends and in-reactor grades are summarized in Table 5.1.

Applications for these materials can vary from automotive bumper fascias and body side moldings to commercial roofing systems. The following outlines the diversity of their performance capability.

1. Mechanical properties: TPOs are available in a wide range of stiffness. With a flexural modulus as low as 34 MPa (5000 psi), the softer TPOs behave and feel like thermoset rubber or leather-like substances, while flexural modulus values as high as conventional PP copolymers are available. The more rigid TPOs are used in stiff applications, such as automotive body panels. These materials retain good impact and abrasion resistance over the entire property range.
2. Thermal properties: Due to the presence of crystalline PP, heat deflection resistance of TPOs is better than many other olefinics and elastomers. With proper stabilization, TPO grades can endure long-term exposure to high temperature without significant loss of properties. The combination of these thermal capabilities makes TPOs particularly suitable for wire, cable, and automotive applications, especially under the hood. The low temperature properties of TPOs are also excellent at retaining their flexibility. This makes TPOs suitable for many outdoor applications.
3. Environmental: As with conventional PP, TPOs have good resistance to solvents, acids, and alkalis, especially for those harder grades which contain more of the crystalline phase. They do not absorb moisture, so they do not need to be dried before processing. They can be formulated to provide excellent resistance to outdoor exposure.

Table 5.1 Selected Property Ranges for Commercial TPOs

Property	Units	Flexible TPO	Stiffer TPO
Melt flow	g/10 min	0.1 - 20	0.4 - 20
Hardness	Shore D	25 - 50	50 - 75
Flexural modulus	MPa (kpsi)	34 - 550 (5 - 80)	550 - 2070 (80 - 300)
Tensile strength	MPa (kpsi)	5.5 - 21 (800 - 3000)	6.9 - 28 (1000 - 4000)
Elongation	%	300 - 800	25 - 800
Gardner impact at −20 °F	J (in-lb)	> 440 (> 320)	54 - > 440 (40 - > 320)

6.3.2   Random Copolymers

Random copolymers are controlled by the same three factors as homopolymers: tacticity, MW, and MWD. However, the introduction of a comonomer presents an additional variable for determining the usual end-use properties and gives new importance to optical properties. The principal reason for making random copolymer is improved opticals.

The introduction of a comonomer into the polymeric chain creates a discontinuity that sharply reduces the crystallization tendency, comparable to a reduction in stereoregularity in homopolymers. The results are a reduction in the rate of crystallization, a lower level of crystallinity, and a reduction in the melting point, all related to the less perfect structure of the chains. The resulting less perfect crystals have a lower density than homopolymer, and thus exhibit a lower refractive index. The difference in refractive index between the crystal and amorphous phases is, therefore, lower, and light is not refracted as readily. The result is lower haze and higher clarity.

Perhaps more important is that the rate of cooling at which the mesomorphic (smectic) phase may be generated is lower for the random copolymers than for homopolymers. Well-quenched films of random copolymers are distinctly clearer than those of homopolymers.

The optical properties of these copolymers may be enhanced further with the use of nucleating agents known as clarifiers. These special organic compounds, besides nucleating the small spherulites desired for improved clarity, also are free of inorganic residues that would contribute to the diffraction that shows up as haze. Thus, they provide the best combination of features for the optical improvement of PP and are widely used in moldings for household applications. The improved optical performance achieved with clarifiers is shown in Table 6.3 [6]. However, clarifiers are somewhat expensive, and some are temperature sensitive.

The second reason for producing random copolymers is to provide a lower melting point, usually for the heat-sealable layer on a film. The reduction in melting point is mainly related to the comonomer content, as illustrated in Fig. 6.6 for ethylene and butene, the most common comonomers with propylene.

Unfortunately, the comonomer behavior is somewhat less ideal than the term "random" suggests. In typical random copolymerizations, the chains exhibit distributions of comonomer content and degree of randomness. Depending on the comonomer reactivity ratio relative to propylene, the polymerization conditions, and the catalytic system used, the distribution of comonomer units along the chains can vary from purely random to alternating segments of homopolymer "blocks," and everything in between. In addition to the desired material (moderate comonomer content, low melting, but crystalline and, therefore, not
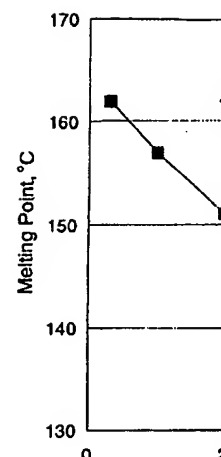

Figure 6.6   Effect of comonom

soluble in hot solvent), son made which would have ve The fraction exhibiting hig but this does not contribute the amount of extractable applications.

The behavior of the mc in this respect. Ethylene, v higher level of extractable temperature and a reductic combination, where the ke modification is achieved, a

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6.3.3   Impact (Hete

The main reason for the de the low-temperature impac with a polymer structure w rubber (EPR), is dispersed

Table 6.3   Optical Effects of Clarifiers

Polypropylene type	Haze of 1.2 mm (50 mil) plaque, %	
	No clarifier	Clarified
Homopolymer	60–65	10–15
Random copolymer	40–45	8–12

Source: Milliken & Co. [6]

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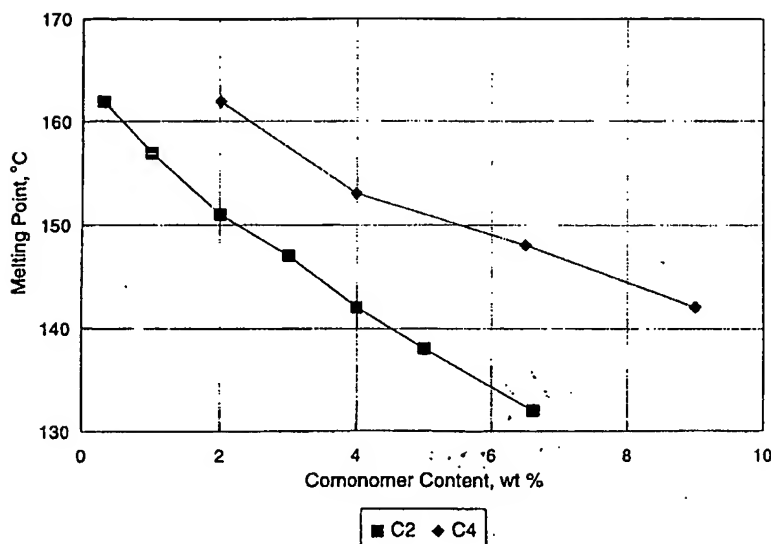
Figure 6.6 Effect of comonomer on random copolymer melting point. Source: Montell Polyolefins

soluble in hot solvent), some high comonomer content, highly random molecules would be made which would have very low melting points and which would be soluble in hot solvent. The fraction exhibiting high comonomer content but low randomness is also highly soluble, but this does not contribute to a lower melting temperature. This becomes a concern because the amount of extractables is a critical factor for regulatory acceptance in food contact applications.

The behavior of the most common comonomers, ethylene and butene, are quite different in this respect. Ethylene, while very effective at melting point depression, also generates a higher level of extractables than does butene. A better balance between the lower melting temperature and a reduction of the extractables is found with an appropriate comonomer combination, where the key advantages of each comonomer can be retained and attractive modification is achieved, as indicated in Fig. 6.7.

It is also worth noting that metallocene catalysts are outstanding in their ability to produce copolymers with very narrow ranges of MW and composition. The difficulties above would be negligible with the use of metallocenes, which are discussed in Section 12.2.

6.3.3   Impact (Heterophasic) Copolymers

The main reason for the development of PP heterophasic copolymers is the improvement in the low-temperature impact strength; thus, the term "impact" copolymers. This is achieved with a polymer structure where an elastomeric phase, usually ethylene-propylene copolymer rubber (EPR), is dispersed uniformly within the PP homopolymer matrix. Although prepared
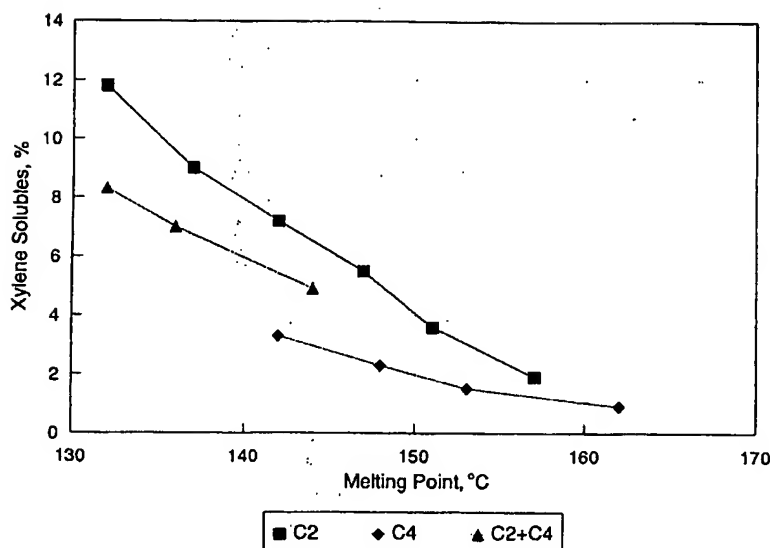
que, %	
	Clarified
	10–15
	8–12

Figure 6.7   Use of combined termonomers to control solubles in random copolymer. Source: Montell Polyolefins
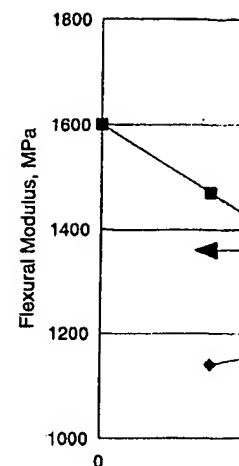
Figure 6.8   Effect of EPR dis Polyolefins

initially by external compounding, reactor-generated impact copolymers were rapidly commercialized in the 1960s. The introduction of the elastomeric component, characterized by a very low modulus, while increasing the impact strength, causes a lowering of the product stiffness, hardness, and tensile strength, as illustrated in Fig. 6.8. As the improvement in the impact strength is related to both the amount and the particle size of the rubbery component, the best compromise between stiffness and impact turns out to be strictly related to the degree of dispersion.

The impact, or heterophasic, copolymers are rather complex; the second phase introduces numerous new factors and limitations in determining the end-use properties. The rubbery phase may vary in amount, size, and composition, in addition to having isotacticity, MW, and MWD affect its properties, as in homopolymers. However, in the dispersed phase, there are some changes: the tacticity is no longer a variable in that the rubber remains essentially amorphous. Further, outside of a desired dispersed/matrix viscosity ratio range, there would be difficulties with the particle size of the rubber, which is discussed below. Thus, while the MW is a "variable," commercial practice dictates that it fall within a range of acceptable values for any given type. Also, MW distribution of the dispersed phase has little influence on the overall resin behavior, so it becomes less important. Comonomer content, however, is an important variable regarding end-use properties.

In impact copolymers (or compounded rubber-toughened PP), the toughening mechanism is related to the generation of many small crazes and the interruption of a propagating fracture in the matrix. When the rubber particles are of the proper size, about 0.4 μm in PP, they initiate many subcritical crazes that absorb significant energy during the stressing of PP and also act to interrupt the crazes before fracture occurs.

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The MW of the EPR p matrix. The right ratio betw shearing force through the c for preventing the reactor processing. Figure 6.9 shc constant matrix viscosity fc results respond differently. determine which test to apr the drop weight method, w. Izod test.

The composition of th good impact strength:

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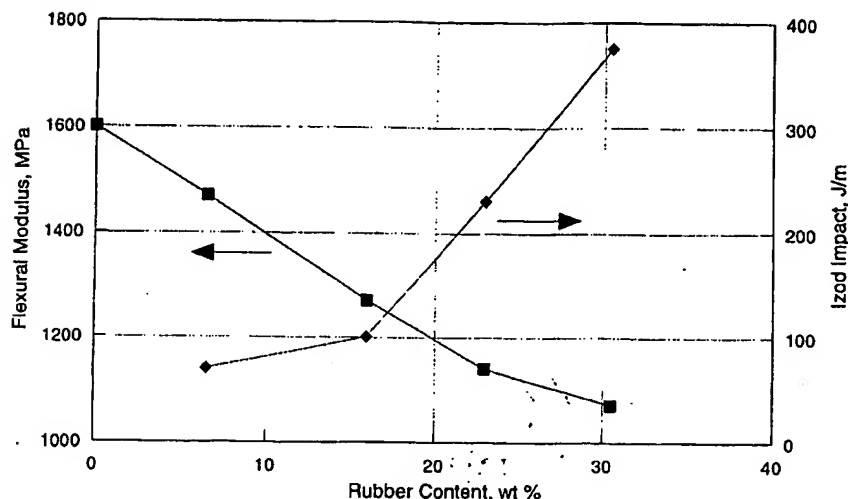3.   amount of crystalline

Figure 6.8   Effect of EPR dispersed in homopolymer matrix on stiffness and impact. Source: Montell Polyolefins

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This mechanism operates above the glass transition temperature of the dispersed phase, and its effectiveness is determined by the nature of the rubbery phase, as well as by its amount, size, and distribution within the matrix. Section 5.3 describes the particulars of this mechanism in more detail, and Section 3.5 describes morphological details.

The nature of the rubber determines the deformation behavior of the dispersed particles and their ability to absorb and redistribute the energy, while the concentration and particle size (and thus the number of particles) define the probability of both initiating crazes and intercepting the fracture line.

The MW of the EPR phase is crucial to controlling the size of the rubber particles in the matrix. The right ratio between the viscosities of the two phases is essential to transferring the shearing force through the continuous phase for dispersing the rubber during compounding or for preventing the reactor-based rubber particles from agglomerating during downstream processing. Figure 6.9 shows the sharp effect of the rubber phase viscosity on impact at constant matrix viscosity for reactor compositions. Note that the Izod and drop weight impact results respond differently. Thus, the intended application for the part must be considered to determine which test to apply. In general, parts with large unsupported panels relate better to the drop weight method, while complex structural parts will reflect more the behavior of the Izod test.

The composition of the EPR phase plays three important roles in the development of good impact strength:

1. Glass transition temperature of the rubber,
2. adhesion between rubber and matrix, and
3. amount of crystalline polyethylene and shrinkage of the rubber phase during cooling.
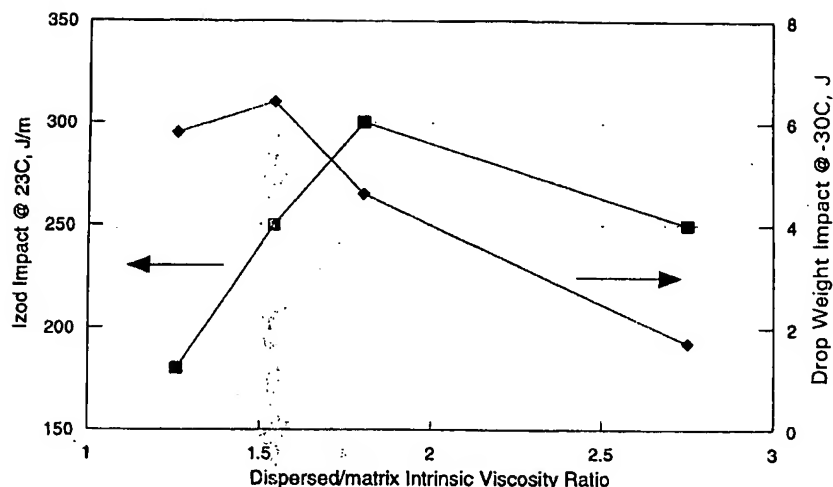
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Figure 6.9 Effect of EPR viscosity on impact. Homopolymer, I.V. = 1.9, EPR content = 15%. Source: Montell Polyolefins

At high propylene content, the T_g of the EPR is high, and the impact improvement is limited. As the ethylene content increases, the T_g drops, and impact improves. At fairly high ethylene levels, PE crystallinity begins to appear within the rubber phase. As a consequence, the rubber particle shrinks more during cooling. This effect reduces stress that otherwise would build up in the matrix, and the tendency to give a stress-whitening effect is reduced, as described in more detail below. The adhesion and impact values reach a maximum. At still higher ethylene content, the rubber becomes stiffer, the dissimilarity between the high-ethylene EPR and the PP matrix increases, adhesion is lost, and impact falls. The maximum in impact occurs at about 50% to 60% C_2 in the EPR rubber, and falls off rapidly on either side [7].

6.3.3.1   Blush Resistance

One advantage of a highly ethylene-rich elastomeric component is the reduction of the stress-whitening phenomenon, or blushing, that results from a small deformation of the part. The blushing is caused by the formation of crazes or voids during deformation, and by the consequent light diffraction. When a heterophasic copolymer melt is cooled, the crystal-lization of the matrix and the associated volume contraction, which is substantially greater than that of the amorphous rubber, creates a compressive stress on the dispersed phase and a comparable tensile stress in the matrix. Consequently, relatively minor deformations raise the tensile stress to the point where crazes form in the matrix.

If an ethylene-rich rubber is used with sufficient ethylene to cause some PE crystal-lization, the volume contraction of the rubbery particles during cooling increases and approaches that of the matrix. This reduces the level of frozen-in stresses and retards the generation of crazes; greater deformation of the part without blushing is then possible. The PE has sufficiently low T_g that impact is not compromised. As the PE tends to gather in the

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6.3.4   High Alloy Co

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6.4   Properties o

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center of the rubber particles, relatively high concentrations are possible without affecting adhesion. The specific morphologies are illustrated in Section 3.5.5.

The addition of a crystalline PE phase has been widely used to eliminate the stress-whitening behavior in impact copolymers through a third phase PE polymerization or via addition of HDPE during compounding. In either case, the structure of the two-component dispersed phase, and the relative amounts of PE and EPR, must be accurately defined to achieve appropriate distribution during downstream operations. It is also important to avoid reaching a composition that would cause a complete detensioning or even development of tensile stress in the rubber, which would result in a reduction of adhesion at the matrix-elastomer interface, with a dramatic decrease in impact resistance.

6.3.4   High Alloy Copolymers

The amount of rubber that may be included in a reactor-generated impact copolymer is strongly dependent on the catalyst and process used. While conventional processes may reach about 50% rubber, later fourth generation catalysts and processes have made possible far higher rubber contents. Catalysts with long-lived activity and the capability of providing PP particles with significantly higher porosities permit the polymerization of much higher rubber content, contained within the particle, without encountering the usual difficulties with reactor fouling and plugging. This containment of the reaction within the protective matrix shell is referred to as the "reactor granule" technology [8]. Rubber content of 70% has been achieved commercially in these materials, which we have called "high alloy copolymers," described further in Section 7.1.8.2. It has been possible to generate cocontinuous phases with the high alloy copolymers, which results in flexural modulus values below 100 MPa and extreme levels of toughness. The toughness of these materials is so high that normal impact measurements are no longer informative. Puncture and tear resistance, and other application-related measures of the toughness, are more appropriate.

The crystallization behavior and toughness of the high alloy copolymers allow processing into films using the air-quenched bubble process [9], or calendering [10], previously impossible with PP. The same control of phase viscosities and interfacial adhesion are necessary to obtain a finely divided rubber phase; in this case cocontinuous layers, as described in Section 3.5.6.

Although conventional PP is not suitable, high alloy copolymers appear well suited for use in biohazard bags, diaper backing films, industrial bags, sheet for roofing and geomembranes, and medical tubing and bags because of the new combinations and exceptional levels of properties offered.

6.4   Properties of Oriented PP

While the variations in the properties of unoriented PP depend strongly on the molecular and morphological characteristics, which has led to the variety of copolymers offered, oriented PP is usually manufactured from homopolymer, and properties depend more on the orientation process than the polymer. Modifications in polymers are most often aimed at improvements in